

Delocalization-Error-Free Density Functional Theory via Fractional Orbital Occupations

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Abstract

By working from a fictitious Kohn-Sham groundstate that violates the conventional aufbau principle, we are able to find a Kohn-Sham exchange correlation functional that is physically motivated, free from delocalization-induced correlation errors and preserves spin symmetry. The functional is derived from a wave function ansatz involving fractional occupations of the highest occupied and lowest unoccupied Kohn-Sham molecular orbitals. In stretched homo- and heteronuclear molecules the method correctly reproduces the groundstate energy and density up to a small, conventional correlation term. It also offers significant improvements over exact-exchange calculations at equilibrium geometries. The approach is robust, straightforward to implement, and an only slightly more expensive alternative to standard Kohn-Sham density functional theory for correlated electronic systems.

Introduction. Electron delocalisation errors and related issues[1–4] have been the subject of intensive study in recent years due to their interesting quantum properties and their importance to molecular modeling, particularly in charge transfer systems. Delocalisation errors arise in most common *ab initio* approximations[5–7], even beyond density functional theory (DFT)[8, 9], and are most prominent when breaking molecular bonds. They are for instance responsible for the dramatic failures (see eg. introduction to Ref. 10) to correctly predict the electron distribution and energetics of heteronuclear dissociation into open-shell fragments, exemplified by the LiH molecule[11].

While much attention has been paid to overcoming the limitations of standard density functional approaches[12–19], the orbital nature of delocalisation suggests that an optimised effective potential (OEP) approach[20, 21] might be generated that intrinsically avoids the errors. The best known OEP approach is the exact-exchange (EXX) approximation within DFT. In EXX, one looks for the Hartree-Fock-like energy of a system using orbital functions φ_i satisfying a common, local Hamiltonian $\hat{h}\varphi_i(\mathbf{r}) = [\hat{T} + V_{\text{KS}}(\mathbf{r})]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$. EXX is known to reproduce many of the important features[22–26] of the true Kohn-Sham (KS) potential in molecular systems containing closed-shell atoms.

However, unless the spin-symmetry is allowed to break[10, 27], the EXX approximation does a poor job of predicting dissociation into open-shell atoms. The majority of the error comes from large delocalisation errors caused by a failure to localize the outermost electrons on the different odd electron number atoms. Instead, the highest occupied molecular orbital (HOMO, H) is doubly occupied, with electrons shared across the two species. This allows “ghost interactions” to cause a static correlation error, with energy cost $1/2\langle\varphi_{\text{H}}^2|v|\varphi_{\text{H}}^2\rangle$ [28] between opposite-spin electrons that should be excluded by the multi-determinant nature of the groundstate.

In this work we will develop a new orbital functional approach that explicitly avoids ghost interactions and delocalisation errors by allowing for fractional occupation of the KS orbitals but integer occupation of ‘quasiorbitals’, defined as linear combinations of the KS orbitals. This scheme differs from other OEP schemes utilising unoccupied orbitals[28–30] in that the unoccupied orbitals are employed to remedy deficiencies of the reference system.

Theory. The approach can be formulated within a fractional occupation based KS

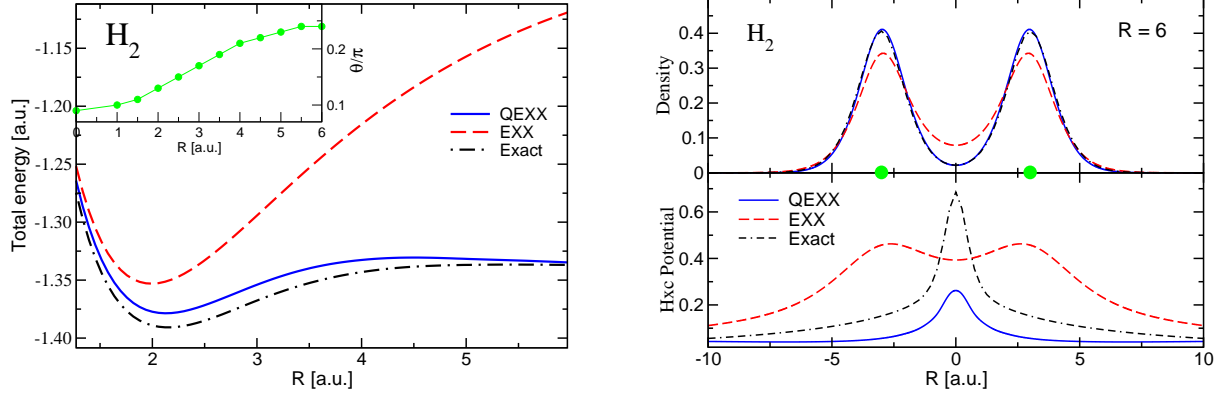


FIG. 1. Left panel: The total energy of the Hydrogen molecule at different separations within EXX and QEXX as compared to the exact results. Right panel: Density and potential at $R = 6$.

DFT[31, 32] in which the density and the kinetic energy functional are written as

$$n(\mathbf{r}) = \sum_i f_i |\varphi_i(\mathbf{r})|^2 \quad \text{and} \quad T_F[n] = \sum_i f_i \langle \varphi_i | \hat{T} | \varphi_i \rangle. \quad (1)$$

The occupation numbers f_i can take any value between 0 and 2 (i.e. they are Fermionic but need not obey the aufbau principle) but are restricted by their sum being equal to the number of electrons. Both the exact density and the exact kinetic energy have this form if the occupation numbers are the natural occupation numbers and the orbitals are the natural orbitals that diagonalize the reduced density matrix. While the present formalism does not attempt to reproduce the exact reduced density matrix, it does allow for more flexibility in determining the exact density from a local potential.

The total energy functional can then be written as

$$E[n] \equiv T_F[n] + \int d\mathbf{r} V_{\text{Ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hxc}}[n] \quad (2)$$

in which $E_{\text{Hxc}} = T - T_F + W$ now differs from its usual definition[5]. Here T is the exact kinetic energy, W is the interaction energy, and V_{Ext} is the external potential. At fixed occupation numbers the orbitals φ_i , used in (1), are determined by optimizing the energy functional. This generates a set of self-consistent equations which we will here call the KS equations. The corresponding effective KS potential is given by

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{Ext}}(\mathbf{r}) + V_{\text{Hxc}}(\mathbf{r}) \quad \text{with} \quad V_{\text{Hxc}}(\mathbf{r}) = \frac{\delta E_{\text{Hxc}}}{\delta n(\mathbf{r})}, \quad (3)$$

where the functional derivative in Eq. (3) is taken with respect to fixed occupations. We note that this potential is different from the standard KS potential with integer occupation

numbers but serves an identical role. The total energy is then calculated from the set $\{f_i, \varphi_i\}$ and the whole procedure is repeated until the minimum energy is found. So far, only a few implementations of a KS approach with fractional occupations (e.g. Refs [4, 17, 33–35]) have been reported. Although the approach has shown some promise it has been held back by a lack of approximations to E_{Hxc} which substantially differ from the standard approximations used in integer occupation KS theory.

In this work we will outline an approximation scheme for E_{Hxc} that intrinsically avoids delocalisation errors and is similar in spirit to the so-called Gutzwiller approach to DFT[36], albeit with a fundamentally different approach to the delocalization process. We will proceed by first considering two electrons only, and generalising later to more electrons. As mentioned earlier, the doubly occupied HOMO orbital in the standard KS formulation of DFT forces both electrons to delocalize across both atoms, whereas the true wave function must localize the two electrons with one on each atom. To reproduce this behaviour we let the electrons occupy *quasiorbitals* which are allowed to localize but are not true orbitals in the sense of being eigenstates of an effective Hamiltonian. The quasiorbitals of a diatomic molecule with spin-degenerate atoms are defined via linear combinations of the HOMO and lowest unoccupied (LUMO) KS orbitals via

$$\psi_A(\mathbf{r}) = \cos \theta \varphi_H(\mathbf{r}) + \sin \theta \varphi_L(\mathbf{r}) \quad (4)$$

$$\psi_B(\mathbf{r}) = \cos \theta \varphi_H(\mathbf{r}) - \sin \theta \varphi_L(\mathbf{r}) \quad (5)$$

with $\theta \in [0, \pi/4]$. These orbitals are normalized but, in general, not orthogonal. At $\theta = 0$ both ψ_A and ψ_B reduce to the KS HOMO orbital and we recover the double occupancy. As θ is increased we mix in more of the LUMO orbital and eventually at $\theta = \pi/4$, ψ_A and ψ_B become orthogonal. The more the KS orbitals are delocalized the more the quasiorbitals will be localized and vice versa. As we will show later, the amount of localization is determined variationally.

We then form Slater determinants of the quasiorbitals. If the ground state is a spin-singlet this requires two Slater determinants so that

$$|\Psi\rangle = \frac{1}{\sqrt{N}} \{ |A\uparrow B\downarrow\rangle + |B\uparrow A\downarrow\rangle \} \quad (6)$$

where $N = 4(\cos^4 \theta + \sin^4 \theta)$ is needed for the normalization. We notice that when $\theta = 0$ this is just the Hartree-Fock (HF) wave function ansatz, while more generally it resembles a

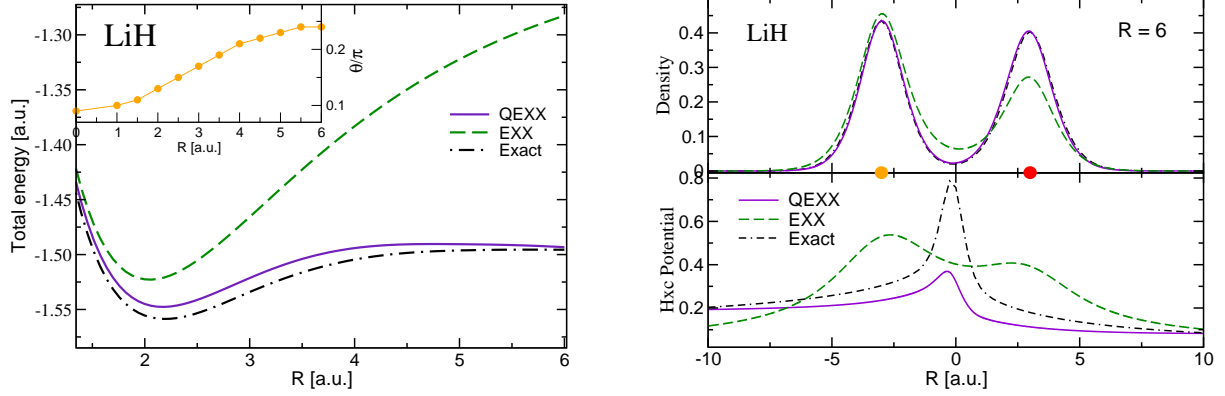


FIG. 2. Left panel: The total energy of the LiH molecule at different separations within EXX and QEXX as compared to the exact results. Right panel: Density and potential at $R = 6$.

Coulson-Fischer ansatz[37]. Taking the expectation value of the full many body Hamiltonian with respect to the wave function in Eq. (6) we find the density and kinetic energy to be

$$n(\mathbf{r}) = f_H |\varphi_H(\mathbf{r})|^2 + f_L |\varphi_L(\mathbf{r})|^2 \equiv \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, \quad (7)$$

$$T_F = f_H \langle \varphi_H | \hat{T} | \varphi_H \rangle + f_L \langle \varphi_L | \hat{T} | \varphi_L \rangle \equiv \langle \Psi | \hat{T} | \Psi \rangle, \quad (8)$$

where the occupation numbers $f_H = 8 \cos^4 \theta / N$ and $f_L = 8 \sin^4 \theta / N$ are related to the fourth power of the expansion coefficients of the quasiorbitals. The interacting energy term is

$$\begin{aligned} E_{\text{Hxc}}^{AB} &= \frac{2}{N} \int d\mathbf{r} d\mathbf{r}' |\psi_A(\mathbf{r})|^2 v(\mathbf{r}, \mathbf{r}') |\psi_B(\mathbf{r}')|^2 \\ &\quad + \frac{2}{N} \int d\mathbf{r} d\mathbf{r}' \psi_A(\mathbf{r}) \psi_B(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \psi_A(\mathbf{r}') \psi_B(\mathbf{r}') \\ &= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n_{HL}^{1/2}(\mathbf{r}, \mathbf{r}') v(\mathbf{r}, \mathbf{r}') n_{HL}^{1/2}(\mathbf{r}', \mathbf{r}) \end{aligned} \quad (9)$$

where $n_{HL}(\mathbf{r}, \mathbf{r}') = f_H \varphi_H(\mathbf{r}) \varphi_H(\mathbf{r}') + f_L \varphi_L(\mathbf{r}) \varphi_L(\mathbf{r}')$ is the density matrix and its square root is interpreted as $n_{HL}^{1/2}(\mathbf{r}, \mathbf{r}') = \sqrt{f_H} \varphi_H(\mathbf{r}) \varphi_H(\mathbf{r}') - \sqrt{f_L} \varphi_L(\mathbf{r}) \varphi_L(\mathbf{r}')$.

Finally, we use (7)-(9) to generate a quasiorbital exact exchange (QEXX) energy expression

$$E_{\text{QEXX}} = T_F + \int d\mathbf{r} V_{\text{Ext}} n + E_{\text{Hxc}}^{AB} \equiv \min_{\theta} E_{\text{QEXX}}^{\theta} \quad (10)$$

which has the same form as Eq. (2). The energy minimization (10) over θ determines the amount of localization of the quasiorbitals $\psi_{A/B}$. Since this functional is derived from a wave function ansatz the energy is guaranteed to be equal or higher than the true energy

E_0 . Furthermore, there is an upper bound given by the EXX energy so that $E_0 \leq E_{\text{QEXX}} \leq E_{\text{QEXX}}^{\theta=0} = E_{\text{EXX}}$.

We will now generalize the QEXX to more than two electrons while still restricting ourselves to two-centered systems like a diatomic molecule. The core electrons are enforced to have integer occupation whereas the HOMO and the LUMO may be fractionally occupied. By expanding the wave function in Eq. (6) it is straightforward to see that it can equivalently be written as a linear combination of two KS Slater determinants of the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\{\sqrt{f_H}|H\uparrow H\downarrow\rangle - \sqrt{f_L}|L\uparrow L\downarrow\rangle\}. \quad (11)$$

From this expression it is straightforward to include the core electrons; we just form the same linear combination of Slater determinants – one with all the core orbitals and the HOMO and the other with all the core orbitals and the LUMO. Evaluating the total energy with this wave function we find $E_{\text{QEXX}} = \int d\mathbf{r}[\hat{T} + V_{\text{Ext}}]n(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} + E_{\text{Hxc}} \equiv \min_{\theta} E_{\text{QEXX}}^{\theta}$ where

$$E_{\text{Hxc}} = E_{\text{Hx}}[n_c, n_c] + E_{\text{Hx}}[n_c, n_A] + E_{\text{Hx}}[n_c, n_B] + E_{\text{Hxc}}^{AB}. \quad (12)$$

Here $E_{\text{Hx}}[n_X, n_Y] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}'[n_X(\mathbf{r})v(\mathbf{r}, \mathbf{r}')n_Y(\mathbf{r}') - \frac{1}{2}n_X(\mathbf{r}, \mathbf{r}')v(\mathbf{r}, \mathbf{r}')n_Y(\mathbf{r}', \mathbf{r})]$ is equal to the normal Hartree and exchange energy and n_c denotes the density matrix of the core orbitals so that $n(\mathbf{r}, \mathbf{r}') = n_c(\mathbf{r}, \mathbf{r}') + f_H\varphi_H(\mathbf{r})\varphi_H(\mathbf{r}') + f_L\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')$. Due to the spin-symmetry, we need only $N/2 + 1$ orbitals for N electrons.

Since QEXX is an orbital functional we have to solve an OEP type of equation

$$\int d\mathbf{r}' \frac{\delta n(\mathbf{r}')}{\delta V_{\text{KS}}(\mathbf{r})} V_{\text{Hxc}}(\mathbf{r}') = \frac{\delta E_{\text{Hxc}}}{\delta V_{\text{KS}}(\mathbf{r})}. \quad (13)$$

to obtain V_{Hxc} . The right hand side is easily evaluated from Eq. (12) (using the functional chain rule $\frac{\delta}{\delta V_{\text{KS}}} = \sum_i \int d\mathbf{r}' \frac{\delta \varphi_i}{\delta V_{\text{KS}}} \frac{\delta}{\delta \varphi_i}$) and the functional derivative in the left hand side is just the linear density response function $\chi_0(\mathbf{r}, \mathbf{r}')$ obtained from the density of Eq. (7).

Let us now analyze the behavior of the new functional for a two electron stretched diatomic system. If the system is symmetric or homonuclear the KS HOMO and LUMO are both automatically delocalized due to the symmetry. As a consequence, when $\theta = \pi/4$ the quasiorbitals are completely localized and, due to the infinitesimal overlap between ψ_A

and ψ_B , we see immediately from Eq. (9) that the interaction energy tends to zero. The functional is thus free from static correlation error.

In the more challenging asymmetric or heteronuclear systems the KS orbitals may or may not be delocalized, depending crucially on the behavior of the KS potential. Without electronic interactions the orbitals would be localized but doubly occupied and hence in the dissociation limit we would find two electrons on the atom with the largest ionization energy and zero on the other. In many cases the electron-electron interaction will prevent this situation due to the strongly repulsive Coulomb interaction and the energy will minimize with one electron on each atom, as for instance in the case of LiH. Standard KS DFT solves this problem by aligning the HOMO of the two atoms via a sharp step in the KS potential. In this way the orbitals delocalize and the doubly occupied HOMO simulates localized electrons. However, all known approximate functionals are only partially able to achieve the step. As a result fractionally charged atoms are found in the dissociation limit – one of the most prominent manifestations of the delocalization error. From Eq. (9) we see that in order for the interaction energy to vanish in the dissociation limit the KS orbitals must again delocalize. Therefore we expect a step feature similar to the one in standard DFT to develop in the QEXX KS potential. We will shortly see that this is achievable and hence both static correlation -and delocalization errors are resolved within the present theory.

Numerical results. In order to test our approach in practice we have applied it to one-dimensional H_2 and LiH, both modeled with soft-coulomb interactions. Thus, the electron-electron interaction is $v(x - x') = 1/\sqrt{1 + (x - x')^2}$ and the external potential is

$$V_{\text{Ext}} = \frac{-Z_1}{\sqrt{1 + (x + R/2)^2}} + \frac{-Z_2}{\sqrt{1 + (x - R/2)^2}} \quad (14)$$

where for H_2 $Z_1 = Z_2 = 1$ and for LiH $Z_1 = 1.2$ and $Z_2 = 1$. The core electrons on the Li atom are frozen and hence LiH is also a two electron system for which we have a numerically exact solution to compare with.

Figure 1 shows the results for H_2 . In the left panel we have plotted the total energy as a function of atomic separation R and compared QEXX to EXX and to exact results. The inset shows θ running between 0 and $\pi/4$. As expected the dissociation limit with $\theta = \pi/4$ is accurately reproduced within QEXX. In addition, we see a substantial improvement around equilibrium and throughout the whole curve. Furthermore, the bond distance is very accurate within QEXX. Notice that the results for QEXX are always above the exact and

below EXX due to the variational nature of the approximation. In the right panel we have plotted the density and the corresponding potential at $R = 6$. The density within EXX is too spread or delocalized whereas within QEXX it is remarkably accurate. The QEXX potential is almost flat but has a peak at the bond midpoint. This behavior is very similar to the standard KS potential, obtained by inversion and plotted in the same figure. The QEXX peak can however be smaller since also the LUMO is exploited when calculating the density.

In Fig. 2 we show the results for the LiH molecule. Apart from the static correlation error, the delocalization error in EXX is apparent. The density is very different from the exact density and by integrating we find that the charge is largely overestimated on the Li atom. By contrast, the performance of the QEXX is exceptional. The quality of the total energy is the same as for the H_2 molecule and the density is almost exactly on top of the exact density. This is correctly achieved by a step in the KS QEXX potential equal in size to the step in the standard exact KS potential. The agreement between the QEXX and KS step size is not surprising as they must both equal the difference in the ionization energy of the two atoms in order to accurately delocalize the KS orbital(s).

Conclusions. By variationally allowing fractional occupations of the KS orbitals we have developed a physically intuitive approach that is able to deal with one of the most challenging situations for common *ab initio* methods. Formulated in terms of quasiorbitals it further gives insights into approaches like density matrix functional theory and fractional occupation based KS theory more generally. The resulting approach is similar to the conventional Kohn-Sham EXX orbital functional, but includes terms coming from the partially occupied KS HOMO and LUMO in the density and energy functionals. It is thus only marginally more computationally demanding than standard OEP-EXX theory but guarantees improved results.

In this work we have only considered spin-degenerate two centered systems, but we will extend the formalism to multi-center and/or orbital-degenerate situations in the near future. We are also considering the implications of the theory on response-based correlation energy calculations like the random-phase approximation.

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